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Theoretical Analysis of Conductance of Molecular Junctions

Submitted by

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A. Summary

The underlying motivation of this project is a fresh look at the theoretical description of electron transport across molecular junctions. In contrast to the current method which is based on the formalism of non-equilibrium Green's function, we treat transport as a dynamical problem in the framework of time-dependent density functional theory (TDDFT). The advantage of our alternative approach is an explicit, more physical description of conductance which is not restricted to linear response and ground-state properties. Our goal is to formulate a benchmark problem for which the theoretical conductance can be unambiguously established, thus elucidating the mechanisms of charge flow across junction-electrode contact, as well as allowing new interpretations of conductance switching behavior that have been observed.

Although the project started on May 30, 2002, actual research did not begin until 9 months later because of personnel availability, the Co-PI moved from MIT to OSU in September 2002, the Research Assistant, a graduate student in the Department of Nuclear Science and Engineering, was not appointed on January 15, 2003, and a Postdoctoral Associate joined the project on June 1, 2003. Presently operating under a no-cost extension, the project is scheduled to end on February 16, 2006.

During this past year, we have continued the development and implementation of a method of propagating Fermi electrons by directly solving the time-dependent Schrödinger equation. A first demonstration of our TDDFT-based scheme is to analyze the transmission and reflection of an electron wave packet from a 1D gold chain through a benzene-(1,4)-dithiolate junction as a scattering problem. We have written a set of computer codes to solve the time-dependent Kohn-Sham equations, (*1, 2*) with an appropriate interaction potential representing the characteristics of the molecular junction. Conductance is then obtained by appealing to Landauer formula. (*3*). Overall our approach is able to treat excited state properties that are not captured by either the Green's function or the Kubo-Greenwood methods. See the following Research Highlights for further details.

Previous reports on project activities have been documented as follows:

1. Statement of Work FY 03, filed 10/24/02
2. Poster presentation, "Theoretical Analysis of Conductance of Molecular Junctions", J.-P.Crocombette, J. Li, X. Lin, X. Qian, S. Yip, DARPA Moletronics PI Meeting, McLean, VA, July 27-30, 2003.
3. DARPA/MTO FY04 Contract Status Report, filed 9/10/03.
4. "Simulation of Electron Transport by Wave Packet Propagation", J, Li, X. Lin, X-F. Qian, S. Yip, presentation at DARPA Moletronics PI Review, June 22-23, 2004, Fairfax, VA.
5. DARPA/ONR FY05 Contract Status Report, filed 9/15/04.

In the remaining period of the project (to February 16, 2006) we plan to complete the

study of electron conductance at a finite voltage bias.

B. Research Highlights

Fermi electron propagation via time-dependent density functional theory

A new computational scheme based on first-principles time-dependent density functional theory is developed to measure the electronic conductance through single-molecule junctions. In this method planewaves are used as the basis set, and core electrons are treated in terms of ultrasoft pseudopotentials. Under the time-dependent local density approximation, valence electron wave functions are propagated in real time by the Crank-Nicolson method. As a demonstration, we compute the scattering process of Fermi electrons from an infinite 1D gold chain by a benzene-(1,4)-dithiolate junction, obtaining a transmission probability of 5% which can be compared to the value of 10% given by the complex band structure method.

Time-dependent density functional theory (TDDFT) provides an efficient framework to solve the time-dependent Schrödinger equation by an *exact* (in principle) mapping between the many-body interacting system and the one-body non-interacting system through an exchange-correlation kernel. High-performance computational codes based on this formalism are currently being implemented in-house to simulate electron wavepacket propagation. At present we have implemented a first-order implicit Euler integration scheme and second-order Crank-Nicolson method. However, we have found that the first-order explicit integration method is unstable. In our current implementation of time-dependent Kohn-Shame equations, the explicit time dependency of nonlocal angular projectors is neglected.

For our first demonstration a test particle (Fermi electron), at the rigid band limit, of a 1D gold chain, is considered. The test electron feels the true potentials of both electrodes and molecular junctions, while the electronic structures of electrodes and molecular junctions are unaffected by the test electron. The initial quantum wave packet is generated by filtering the Fermi electron wavefunction with a Gaussian window, which approaches the true wavefunction limit as the Gaussian width gets large. In our test runs, we find that such a Fermi electron wave packet, traveling at an initial group velocity of 10 Å/fs, retains its Gaussian shape with only small broadening for ~ 4 fs, with 100% transmission probability.

Two systems have been investigated.

1. Gold Chain (Fig. 1, see Appendix E for all the figures.)

Standard groundstate calculations are performed by using the CAMPOS/Dacapo's DFT package. (*4*) We consider two equivalent 1D configurations under the periodic boundary condition (pbc), a 1-Au atom chain with a 64 Monkhorst-Pack k-sampling points and a 12-atom Au chain with the Γ point sampling. The bond length of Au-Au is fixed at 2.88 Å along the x direction of the cubic pbc box.

Fig. 2 shows the band structure of the 1D gold chain. The Fermi level is located at -6.65 eV (dotted line). The projected density of states analysis of Fig. 3 indicates that the Fermi level are composed of *s* and p_x angular channels in this 1D chain. In other words, *d* angular channels contribute little to the conductance. Moreover, due to time inversion symmetry, the Fermi level is doubly degenerate. Therefore, one may construct a moving Fermi wave packet with a constant momentum from these two stationary degenerate eigenfunctions, one as the real part and the other as the imaginary part. To estimate the Fermi velocity, we create a small sinusoid modulation on the ground state charge density profile and observe the propagation of the modified profile in time (Fig. 4). From the slope of the pink line, we obtain a group velocity of 10 Å/fs, which is consistent with the band structure estimates of Fig. 2.

From this simple test case, we learn: a) the Fermi electrons of a 1D gold chain are *s* and p_x electrons; b) these *s*-p_x electrons move at a speed of 10 Å/fs; c) if the Fermi level can be lowered by 1 eV (for instance, via external chemical potential pinning), *d* electrons would play a more significant role, while their group velocities are still very low; and d) if the Fermi energy can be raised by 1 eV, the group velocity of the *s*-p_x electrons can increase significantly.

2. Gold chain connected with benzene-(1,4)-dithiolate junction (Fig. 5)

It has been widely recognized that mesoscopic electrical conductance mainly comes from electrons around the Fermi levels of the electrodes. Fermi electron wavefunctions of the 1D gold electrode are taken from DFT results described in the previous section. Small test electrons are again propagated along the chain direction with periodic boundary conditions mimicking the infinite long gold chain. The time sequences are highlighted in the test electron charge isosurface plots of Fig. 6 and the profile summation plot of Fig. 7, over the planes (the y-z planes) perpendicular to the propagation direction (x-direction). It is evident that there is finite electron transmissions. Quantitatively, we determine the transmission probability as the proportion of test electron density which arrives at the target region, namely, the space to the right of the right S atom at the instant the reflecting image wavefunction enters the pbc box from the right. As shown in Fig. 7, one sees plateaus of transmission probability, followed by sharply increasing peaks. These peaks are due to reflected electrons entering the region on the right hand side because of periodic boundary condition. In this way, a transmission of 5% is obtained for this particular molecular junction. This value is roughly consistent with the value of about 10% given by the complex band structure method at zero bias voltage. We find the main contributions to the transmission come from high-lying π electronic channels of the benzene ring. When scattered by the junction, the Fermi electron wave packet becomes strongly delocalized throughout the 1D gold chain. In this sense, electronic conductance through a non-conducting molecular junction is similar to the quantum tunneling

through barriers, although here the barriers may vary in time as the incoming Fermi electron interacts with junctions.

We have calculated the transmission coefficient of a Fermi electron propagating through a single molecular junction by combining degenerate levels near the Fermi energy. It is quite clear that the benzene-(1,4)-dithiolate junction has a small conductance at zero bias voltage. Our result is considered reasonable since it of the same order as the complex band structure calculations. In the work ahead we will consider treating finite bias voltage, more efficient way to approach steady state, and time-dependent interacting potentials. The question of time-dependent exchange correlation kernel looms as a considerable challenge.

References Cited

1. W. Kohn, *Physical Review Letters* **76**, 3168 (April 22, 1996, 1996).
2. R. M. Dreizler, E. K. U. Gross, *Density Functional Theory An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1990), pp. 302.
3. R. Landauer, *IBM. J. Res. Dev.* **1**, 223 (1957).
4. *http://www.fysik.dtu.dk/CAMP/dacapo.html*.

B. Publications and Manuscripts in Preparation

1. Xi Lin, Ju Li, Elisabeth Smela, and Sidney Yip, *Polaron-Induced Conformation Change of a Single Polypyrrole Chain: An Intrinsic Actuation Mechanism*, International Journal of Quantum Chemistry, **102**, 980-985 (2005).

2. Xi Lin, Ju Li, and Sidney Yip, *Controlling Bending and Twisting of Conjugated Polymers via Solitons*, submitted to Science.

3. Xi Lin, Ju Li, Clemens Foerst, and Sidney Yip, *Multiple Self-Trapped Soliton States in Trans-Polyacetylene*, in preparation.

4. Xiaofeng Qian, Ju Li, Xi Lin, Sidney Yip, *Fermi Electron Propagation through Single-molecule Junction via TDDFT*, in preparation for submission to Physical Review B.

D. Personnel

Besides the Principal Investigator Professor Sidney Yip and the Co-PI Professor Ju Li at Ohio State University, the project supports a graduate student, Mr. Xiaofeng Qian, in the Department of Nuclear Engineering at MIT. The research team also includes Dr. Xi Lin, a Postdoctoral Associate in the group, as a collaborator who is not supported by the project.

E. Appendix

In this appendix we collect all the figures that were discussed in section Research Highlights.

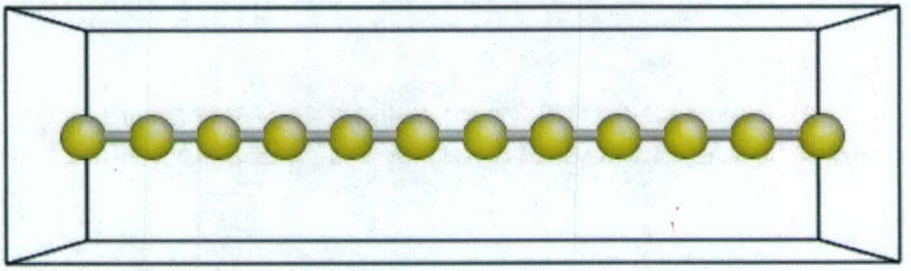

Figure 1. Gold Chain configuration in TDDFT propagation

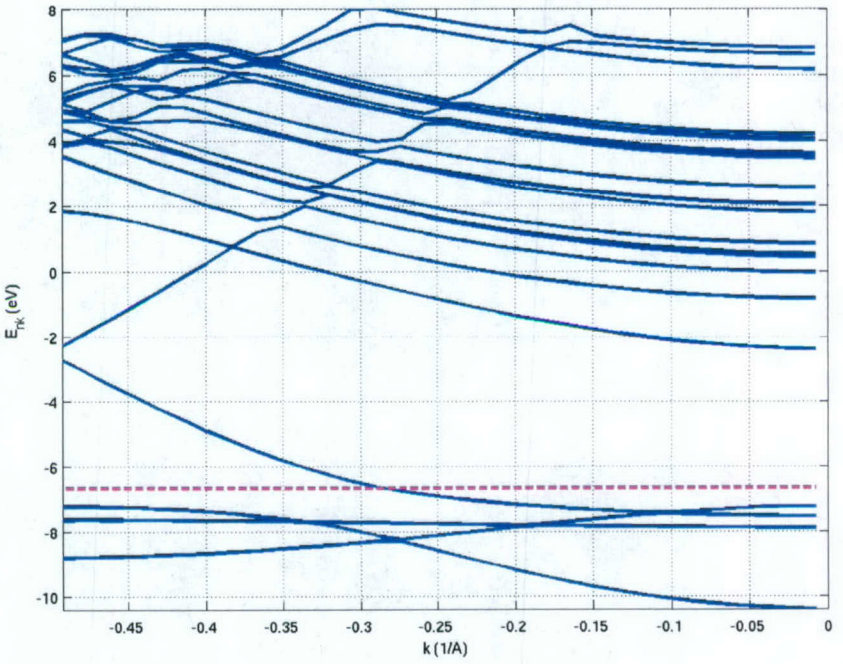

Figure 2. Band structure of gold atom in the chain configuration with a 64 k-point sampling

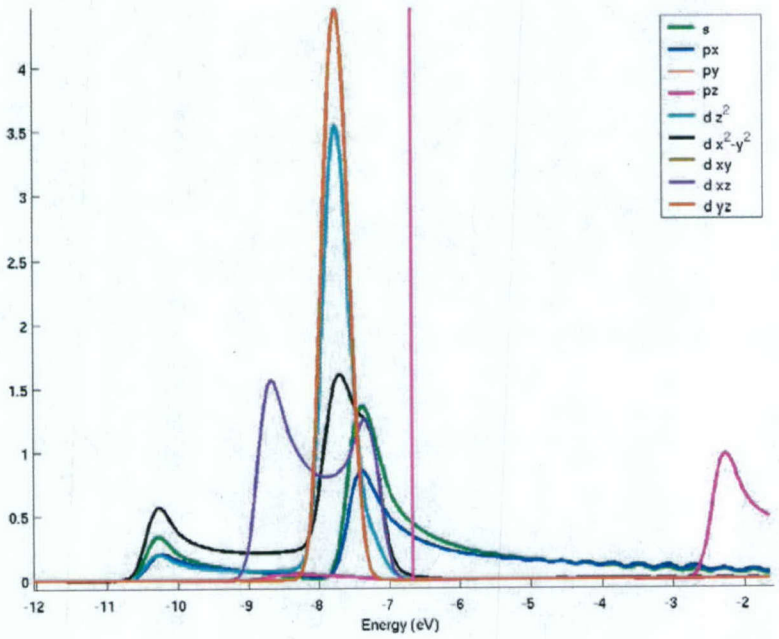

Figure 3. Projected density of state analysis of gold chain. Note that the angular channels of Fermi electrons are mainly S and P_x.

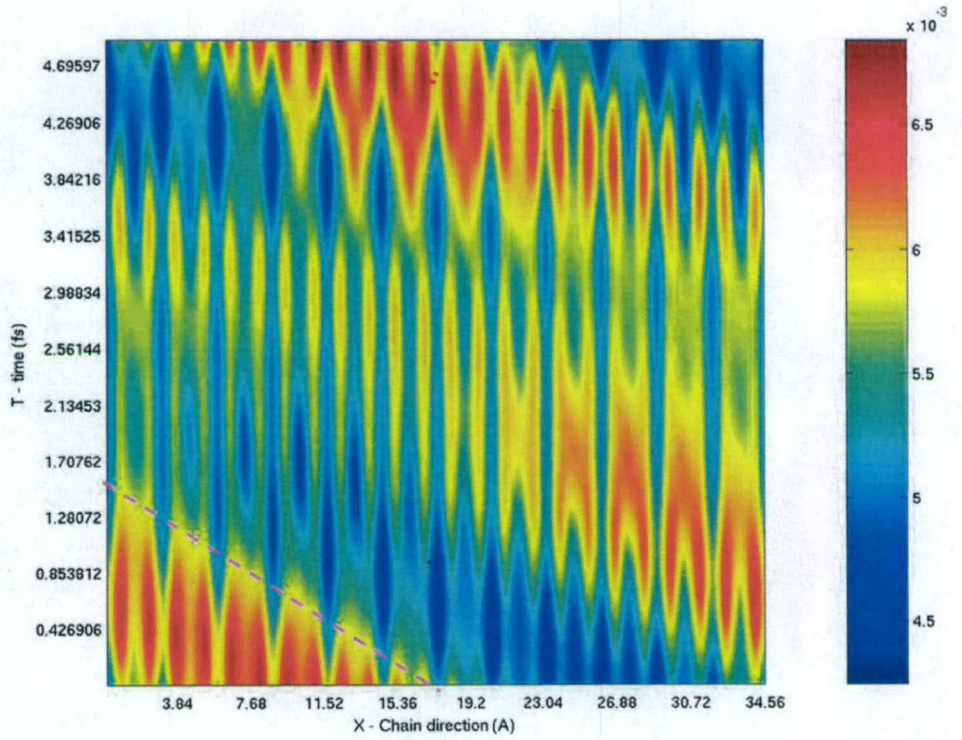

Figure 4. Fermi electron of gold chain propagation with tiny sin shape modulation. Note that the slope of the pink line indicates the group velocity of this Fermi electron.

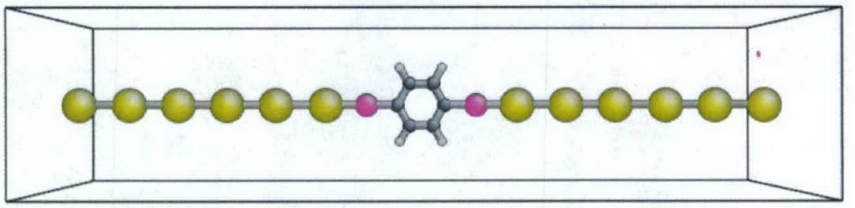

Figure 5. Gold chain connected with benzene-(1,4)-dithiolate junction

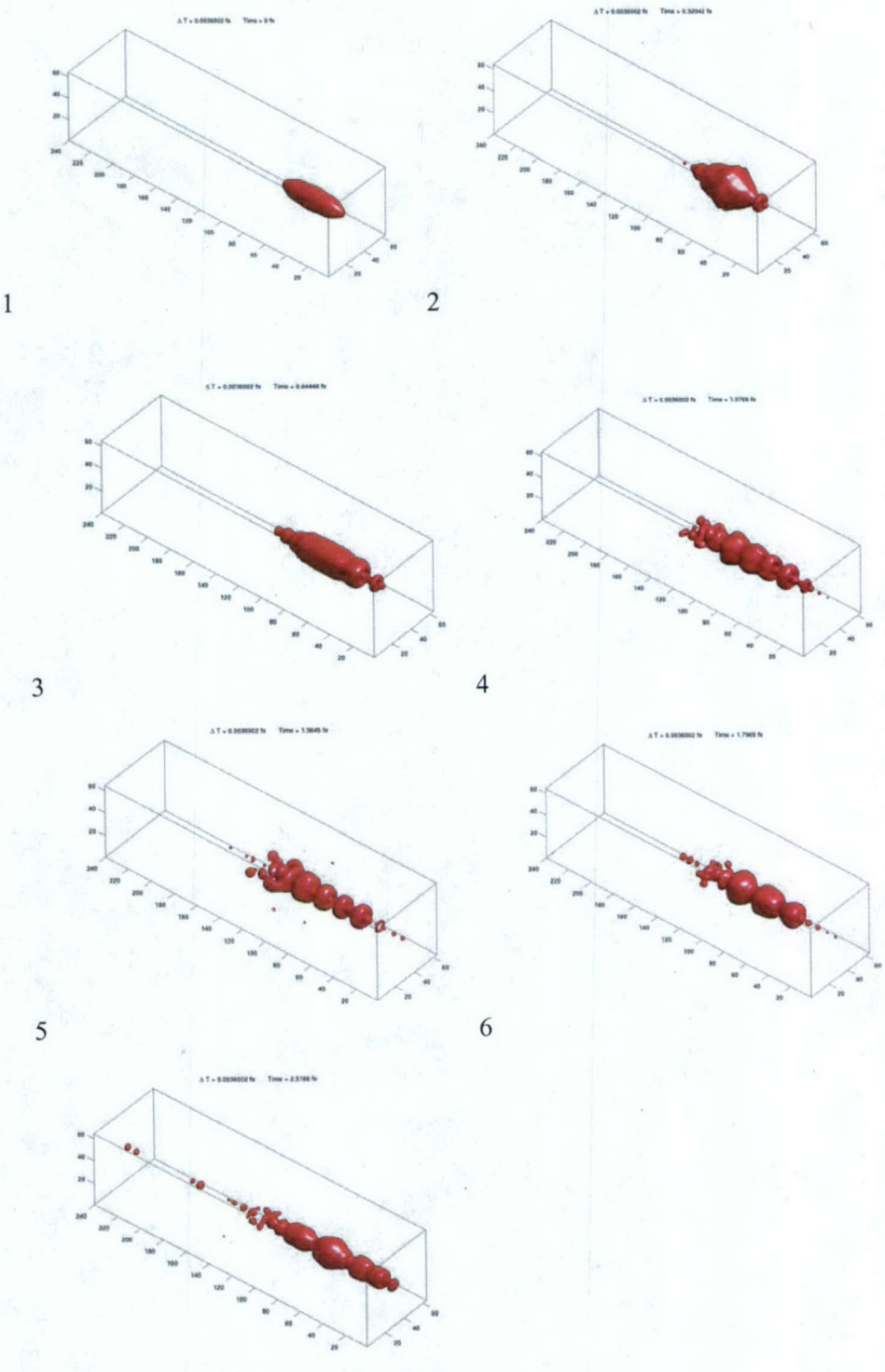

Figure 6. Isosurface plot of the propagating Fermi electron

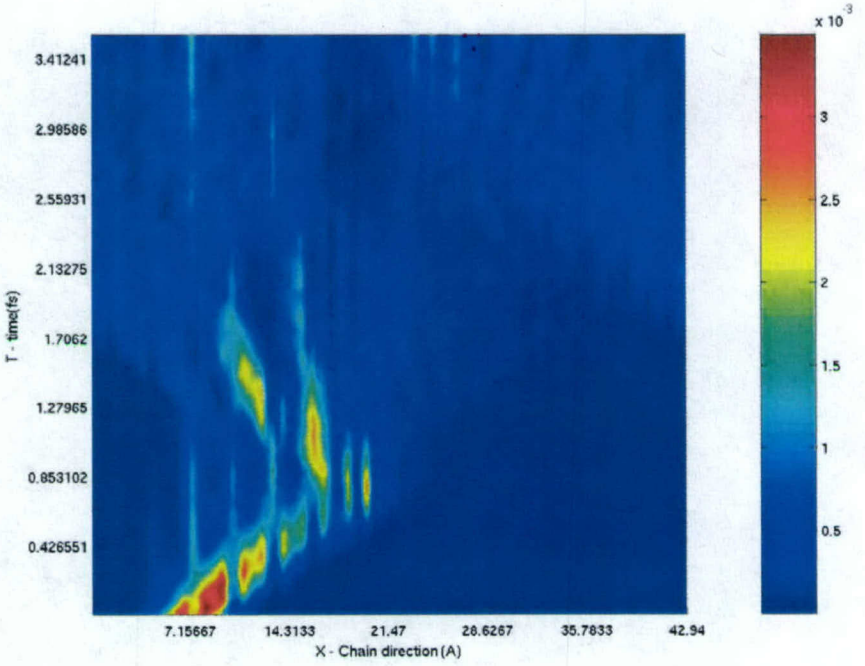

Figure 7. Fermi electron propagation through a Au chain connected with benzene-(1,4)-dithiolate junction.

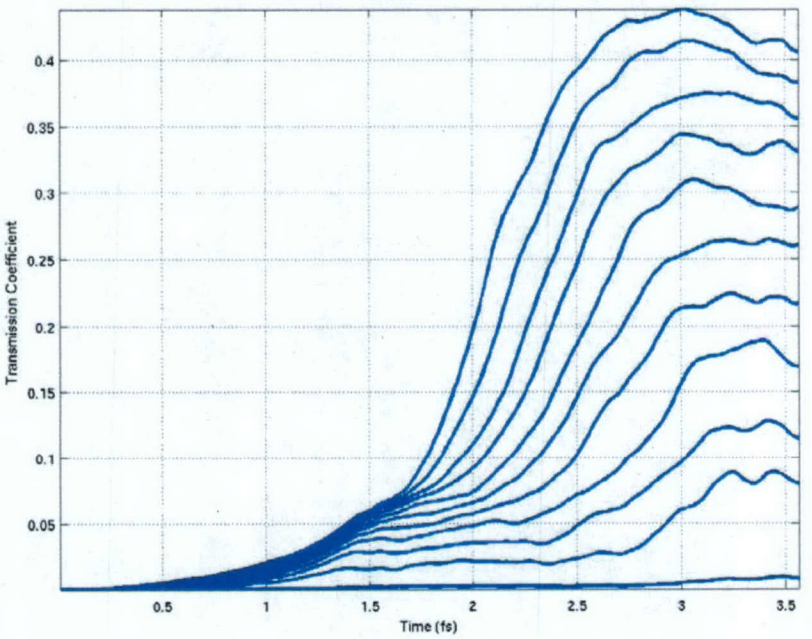

Figure 8. Transmission coefficient plot of Fermi electron propagation through molecular junction. Note that plateaus form around 1.5-1.7 fs with sharp increase followed due to reflection of electron density in the periodic boundary condition; plateaus indicate the total transmission coefficient is around 5%.